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Evaluation of corrosion resistance of magnesium alloy ZK10 coated with hybrid organic–inorganic film including containers

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ABSTRACT

This study is focused on the corrosion protection of magnesium alloy ZK 10. Coatings consist of cross-linked polymers based on bisphenol A diglycidyl ether as well as organic modified silicates including cerium molybdate containers were synthesized and applied to the metal alloys. The films were investigated for their morphology and nanomechanical properties. Corrosion studies were made using open circuit potential, cyclic potentiodynamic polarization and electrochemical impedance spectroscopy after immersion in 0.5 M sodium chloride solution. The evaluation of possible self-healing effect was made via formation of artificial defect on the surface of the coatings and consequently exposure to corrosive environment.

1. Introduction

Magnesium and its alloys is used in a wide range of applications due to its low density (it is only 65% that of aluminum and 25% that of iron) as well as its high strength/weight ratio [1,2]. On the contrary, engineering applications of magnesium have been limited mainly due to the poor corrosion properties of magnesium alloys [3]. Several coating applications have been developed in order to improve the corrosion resistance of magnesium and its alloys, such as electrolytic plasma oxidation [4,5], inorganic pre-treatments [6,7], spin and dip coating methods [8–10], ion beam-assisted deposition [11], anodizing process [12], vapor phase method for self-assembled monolayer [13], etc.

A very promising application for corrosion protection of magnesium and its alloys is hybrid organic–inorganic sol–gel coatings. Ishizaki et al. applied superhydrophobic surfaces on Mg alloy AZ31 with nanostructured cerium oxide film and fluoroalkylsilane molecules [14]. Studies on the protection of Mg alloy AZ91D have been made by Hu et al. who used composite coatings which consisted of a molybdate conversion coating and three layers of silicon sol–gel coatings [15]. Shi et al. prepared sol–gel coatings for the same alloy using 3-glysicoxypropylthrimethoxysilane and tetraethoxysilane as precursors, diethylentriamine as curing agent and 2-methyl piperidine as inhibitor [16]. Furthermore, Tan et al. synthesized multilayer sol–gel coatings for corrosion protection of AZ91D based on 3-methacryloxypropyl trimethoxysilane, 3-meraptopropyl trimethoxysilane and ethanol. The multilayer approach was found to significantly improve the corrosion resistance of Mg by reducing levels of porosity [17]. Ferreira et al. developed a complex anticorrosion protection system for ZK30 magnesium alloy that based on an anodic oxide layer loaded with corrosion inhibitors in its pores which was then sealed with a sol–gel hybrid polymer. The developed complex anticorrosion coating beneficially combines increased corrosion resistance of the magnesium substrate due to the additional protective oxide layer and the greater adhesion of thin sol–gel coating to the porous anodized surface, while also conferring active protection properties owing to the corrosion inhibitor securely impregnated in the porous reservoirs [18]. Improved corrosion protective properties have also obtained via the application of epoxy based coatings on magnesium alloys [19,20].

Nanoindentation and nanoscratch tests have been widely applied for the measurement of mechanical properties of coatings and thin films [21–24]. The nanoindentation test can provide information about the mechanical behavior of the material when it is being deformed at the sub-micron scale. The method developed by Oliver and Pharr allows determining the hardness and the elastic modulus from the nanoindentation load–displacement data [25].

In this paper, we report the corrosion resistance and nanomechanical performance of hybrid organic–inorganic coatings including containers applied to magnesium alloy ZK10. The containers consist of cerium molybdate and were loaded with 2-mercaprobenzothiazole (MBT). Not only the hybrid coatings were evaluated for their corrosion protective behavior, but the contribution of

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each parameter such as containers, corrosion inhibitor was estimated as well. Furthermore, their nanomechanical properties, mechanical integrity in terms of plasticity and wear resistance were examined, too.

2. Materials and experimental details

2.1. Materials and reagents

Magnesium alloy ZK10 (composition: 1.35–1.45 wt% Zn, 0.5–0.6 wt% Zr, ⩽0.25 wt% Mn, 0.2–0.25 wt% Rh and the rest is Mg) was obtained from Alubin – Israel [26]. All chemicals were of analytical reagent grade. MBT (Sigma–Aldrich, St. Louis, USA), cerium (III) acetylacetonate ($Ce(acac)_3$, Sigma–Aldrich, St. Louis, USA), polyvinylpyrrolidone (PVP, average molecular weight: 55000, Sigma–Aldrich, St. Louis, USA), potassium persulfate (KPS, Sigma–Aldrich, St. Louis, USA), sodium dodecyl sulfate (SDS, Sigma–Aldrich, St. Louis, USA), aceton (Sigma–Aldrich, St. Louis, USA), USA), *N*-(2-aminoethyl)-3-(trimethoxysilyl)propylamine (Z 6020, Sigma–Aldrich, St. Louis, USA), epoxy resin based on Phenol 4,4′-(1-methylethylidene) bis-("Araldite GY 257", GY 257, Ciba-Geigy), 2,2′-diaminodiethylamine (HY 943, Sigma–Aldrich, St. Louis, USA) were used without further purification. Styrene (Sigma–Aldrich, St. Louis, USA) was double distilled under reduced pressure prior to use.

2.2. Synthesis of containers

The production of cerium molybdate containers was based on a two-step process. The method of emulsion polymerization was used to produce anionic polystyrene latex, used as core particles. For this purpose, the reaction was carried out in a 500-cm^3 container under the condition listed in Table 1. To eliminate the effects of oxygen, the solution was purged with nitrogen before the process was initiated. The polymerization process lasted for 12 h. The resulting dispersions were centrifuged at 14000 rpm for 30 min, the supernatant solutions were discarded, and then the particles were resuspended in doubly distilled water using a sonicator. This process was repeated three times. The polystyrene lattices were coated via the sol–gel method to form a cerium molybdate layer. The sol–gel coatings were prepared by controlled hydrolysis of $Ce(acac)_3$ and sodium molybdate aqueous solution in the presence of polystyrene latex and PVP. These dispersions were aged for 3 days at 96 °C (Table 2). The resulting dispersions were centrifuged at 14000 rpm for 30 min, the supernatant solutions were discarded, and then the particles were resuspended in doubly distilled water with a sonicator. This process was repeated three times, and the purified powders were dried in a desiccator. The production of cerium molybdate containers included the removal of polystyrene cores by calcination. Initially, the coated spheres were placed on a glass slide and dried, first at room temperature and then for 1 h at 60 °C. Then, the composite was calcinated for 4 h in air in a furnace at 550 °C. The heating rate was 10 °C min^{-1}. The containers exhibited an average diameter of 230 ± 20 nm [27].

Table 1
The conditions used in the preparation of polystyrene latex at 80 °C.

Material	Quantity (g)
Styrene	40.0
Potassium persulfate	5.2
Sodium dodecyl sulfate	0.85
Water	1850
Spheres' size (nm)	200 ± 10[a]

[a] Determined by Scanning Electron Microscopy analysis.

Table 2
Conditions of preparation of coated spheres.

Material	Quantity (g)
Polystyrene	40.0
Polyvinylpyrrolidone	40.0
Cerium (III) acetylacetonate	24.0
Sodium molybdate	2.0
Water	3000
Spheres' size (nm)	240 ± 20[a]

[a] Determined by Scanning Electron Microscopy analysis.

The obtained cerium molybdate containers were loaded with the corrosion inhibitor MBT. The process for the loading was the following. Firstly, a saturated solution of MBT in acetone was prepared. An amount of cerium molybdate containers was placed in a sealed container. The air of the inner side of the containers was eliminated with a vacuum system. Then, the saturated solution of MBT in acetone was inserted in the sealed container and the whole mixture was stirred at room temperature for 2 h. Finally the cerium molybdate containers loaded with MBT were collected through centrifugation and drying under vacuum at 60 °C overnight. The containers were 58.08% w/w loaded with MBT [28].

The containers consist of cerium molybdate because cerium cation and molybdate anion are corrosion inhibitors [29] and were loaded with 2-mercaprobenzothiazole (MBT) which is also a corrosion inhibitor [30].

2.3. Coating preparation

The synthesis of the coating includes the hydrolysis of the organic modified silicate, Z 6020, in absolute ethanol for 1 h (solution A). Simultaneously, the epoxy resin GY 257 was dissolved in absolute ethanol (solution B). After that, solutions A and B were intermixed formatting solution C. Then, HY 943 was dissolved in 25 ml acetone (solution D). Finally, solutions C and D were intermixed and stirred for 8 h (solution E). The preparation of the hybrid coating including inhibitor without containers (HybridCoat-MBT) includes the addition of 1.5 wt% MBT in the solution E under vigorous stirring 1 h before the dip coating process. The preparation of the hybrid coatings incorporating containers empty (HybridCoat-nc) or loaded (HybridCoat-ncMBT), includes the addition of 10 wt% containers in the solution E under vigorous stirring 1 h before the dip coating process.

2.4. Dip coating process

Four different types of coatings were prepared. At first, coatings free of inhibitor or containers were synthesized (HybridCoat). Then, coatings were prepared that had incorporated only inhibitor in a free form (not encapsulated) (HybridCoat-MBT) or empty containers (HybridCoat-nc). Finally, coatings were fabricated that had containers loaded with inhibitor (HybridCoat-ncMBT). The panels were dip coated into the container solution for six times with a withdraw rate of 32 cm/min. The panels remained in the solution for 1 min. Then, the coated panels were heat treated at 70 °C for 4 days. The ZK10 magnesium alloys panels had been previously cleaned, under the following conditions. First of all, the panels were inserted into 96 v/v% ethanol for 20 min at room temperature, under sonication. After that, the panels were rinsed with distilled water and inserted into a degreaser solution (40 g/L NaOH, 20 g/L Na_2CO_3, 0.1 wt% sodium lauryl sulfate, water) for 10 min at 70 °C. Then, the panels were inserted in distilled water for a few minutes at 40 °C. The next step included the insertion of the panels in hydrofluoric acid 10 wt% for 20 min at room temperature. Finally, the panels were rinsed with distilled water and left to dry in air.